

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
9 January 2003 (09.01.2003)

PCT

(10) International Publication Number  
**WO 03/002854 A1**

(51) International Patent Classification<sup>7</sup>: F01N 3/08, 3/20,  
B01D 53/94, F01N 3/027

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(21) International Application Number: PCT/EP02/06249

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,  
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,  
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,  
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,  
VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 21 June 2002 (21.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
01202457.6 26 June 2001 (26.06.2001) EP  
60/300,456 26 June 2001 (26.06.2001) US  
01202456.8 26 June 2001 (26.06.2001) EP  
60/300,432 26 June 2001 (26.06.2001) US

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,  
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent  
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,  
NE, SN, TD, TG).

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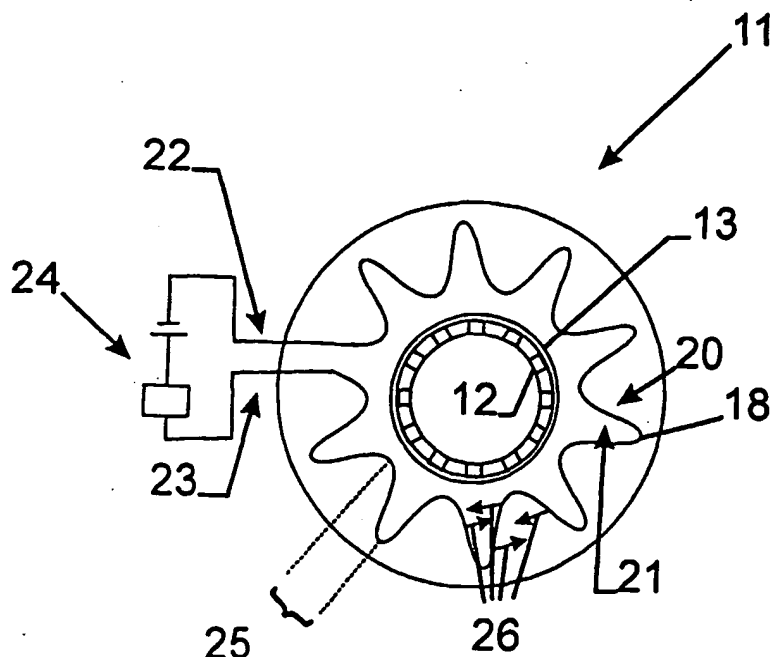
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**Published:**

- with international search report
- before the expiration of the time limit for amending the  
claims and to be republished in the event of receipt of  
amendments

[Continued on next page]

(54) Title: A METHOD OF DESULFATION OF NO<sub>x</sub>-ADSORBERS



(57) Abstract: The invention relates to a method of desulfation of NO<sub>x</sub>-adsorbers (11) in a diesel exhaust system, comprising the steps of periodically increasing the temperature of the electrically conductive substrate (18) of the NO<sub>x</sub>-adsorber (11) above the decomposition temperature of the adsorbed S-comprising compounds by providing electric current to the electrically conductive substrate (18).

WO 03/002854 A1



*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## A METHOD OF DESULFATION OF NO<sub>x</sub>-ADSORBERS

### Field of the invention.

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The present invention relates to a method of desulfation of NO<sub>x</sub>-adsorbers in a diesel exhaust system. The invention further relates to a NO<sub>x</sub>-adsorbing element able to perform this method, and an NO<sub>x</sub>-adsorbing unit, comprising such NO<sub>x</sub>-adsorbing elements.

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### Background of the invention.

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Reducing the amount of NO<sub>x</sub> in lean exhaust gases is commonly known in the art. The following catalytic approaches were investigated: NO decomposition catalyst, selective catalytic reduction with ammonia (SCR), selective catalytic reduction with hydrocarbons (DeNO<sub>x</sub> or lean NO<sub>x</sub> catalyst).

20

Although initially promising, catalytic decomposition of NO has proven difficult to realize. The decomposition is subject to inhibition by water, is very sensitive to poisoning by SO<sub>2</sub>, is effective only at low space velocities, and the catalyst activity and selectivity are not satisfactory. Selective catalytic reduction (SCR) of NO<sub>x</sub> can be realized if a reducing agent is injected into the gas upstream of the catalyst bed. SCR processes utilizing nitrogen containing reductants such as ammonia or urea. Disadvantages of SCR include high capital and operating costs, space requirements, generation of ammonia emissions, and fouling of equipment with ammonium sulfate (hazardous waste).

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In the selective catalytic reduction with hydrocarbons (deNO<sub>x</sub>-catalysts), the urea or ammonia of the SCR system is replaced by hydrocarbons. The developed deNO<sub>x</sub> catalysts have specific drawbacks, related primarily to narrow temperature windows, insufficient thermal durability and/or sulfur tolerance. More importantly 10-20% NO<sub>x</sub> conversions of the system on regulated test cycles have been reported. deNO<sub>x</sub> catalysts are not currently seen as technology capable of coping with the stringent future emission targets.

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5 To overcome the situation of low NOx conversions of the deNOx catalysts under lean conditions, so-called NOx adsorbing compounds were incorporated. These compounds were supposed to adsorb NOx during periods of low exhaust gas temperature, when deNOx catalyst activity was low, and to release it at temperatures which could favor the selective reaction with hydrocarbons.

10 The idea above, addition of NOx adsorbing compounds, coupled with the three-way catalyst result is the NOx adsorber. The concept of the NOx adsorber/catalyst, also referred to as the NOx trap, has been developed based on the acid-base washcoat chemistry. NOx adsorbers are materials which store NOx under lean combustion conditions (low air to fuel ratio) and release and catalytically reduce the stored NOx under rich combustion conditions. The NOx adsorber can achieve 90% NOx reduction efficiency over relative wide temperature window.

The catalyst washcoat combines three active components:

- (1) an oxidation catalyst, eg Pt
- (2) an NOx adsorbant eg BaO
- 20 (3) a reduction catalyst eg Rh.

The system cycles through two stages of operation, including

- (1) storage (chemisorption) of NOx in the catalyst washcoat during lean combustion operation
- 25 (2) regeneration of the trap through desorption and non-selective catalytic reduction of NOx during periods of rich combustion operation.

30 The two stages of operation, storage and regeneration, essentially comprises in total 3 steps:

- (1) NOx emissions from the diesel engine are typically composed of 90-95% nitric oxide, NO. The NO is oxidised as much as possible to NO2 over an appropriate oxidising catalyst, eg Pt

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- 5 (2) Adsorbing the obtained  $\text{NO}_2$ , as well as the remaining NO, by the adsorbing compound, eg BaO, in the form of an inorganic nitrate. As an example, when BaO is used, NO and  $\text{NO}_2$  is adsorbed or so-called "trapped" providing  $\text{Ba}(\text{NO}_3)_2$ .  $\text{NO}_2$  is to be provided as much as possible, since  $\text{NO}_2$  is adsorbed best by the NOx-adsorbing compounds.
- 10 (3) Regeneration of the NOx adsorber involves reaction mechanisms virtually identical to those found in the gasoline three-way catalyst. A reductant, presumable carbon monoxide or hydrocarbons, reacts with NOx in the absences of oxygen to form elementary nitrogen. Therefore periodic "rich" conditions, a rich air to fuel mixture, are necessary. In general, such enrichment of the exhaust gases with additional HC, could be realized by two methods: (1) Injection of hydrocarbons,
- 15 preferable diesel fuel, into the exhaust system upstream of the catalyst or (2) Late-in-cylinder injection in a common rail fuel system (or merely late injection timing in conventional fuel systems).
- 20 Enrichment of the exhaust gases is necessary in order to obtain the desadsorption of the trapped N-comprising compounds.
- 25 A severe problem is the presence of S and S-comprising compounds in the diesel fuel and engine lubricant oil. Due to the combustion, these S-comprising compounds are combusted essentially to  $\text{SO}_2$ . In the presence of the oxidation catalyst, these compounds are oxidized to  $\text{SO}_3$  and forms stable sulfates with the NOx adsorbing compounds. The adsorption of sulfur compounds is preferential over the adsorption of NOx. Sulfates derived from the known NOx storage materials are more
- 30 thermally stable than the corresponding nitrates. They do not decompose at conditions that are usually encountered during adsorber operation, including both the adsorption NOx regeneration cycles. The necessary temperatures cannot be obtained. As a result, the adsorber/catalyst performance gradually declines as fewer sites are

available for NOx adsorption. The S-comprising compounds stay present on the NOx adsorber. Higher levels of sulfur in fuel results in faster and more severe deactivation.

Even sulfur levels less than 10 ppm eventually lead to NOx adsorber poisoning, not to mention sulfur contribution from the engine lubricant oil. Ultra low sulfur fuels are the necessary condition for implementation of this technology, but even if such fuels are available NOx adsorbers are still likely to require some form of desulfation mechanism.

#### Summary of the invention.

The present invention relates to a method of desulfation of NOx-adsorbers in combustion systems, comprising the steps of

- Providing an electrically conductive substrate comprising metal fibers, an oxidizing catalyst, a reducing catalyst and a NOx-adsorbing compound;
- executing a loading step by passing the exhaust gasses from the diesel exhaust system through the electrically conductive substrate, at least partially oxidizing S-comprising compounds and at least partially adsorbing oxidized S-comprising compounds as adsorbed S-comprising compounds on the NOx-adsorbing compound;
- executing a desulfation step by increasing the temperature of the electrically conductive substrate above the decomposition temperature of the adsorbed S-comprising compounds by providing electric current to the electrically conductive substrate.

With combustion system is meant a system which burns or combusts fuels, e.g. diesel, such as diesel burners or diesel engines, stationary or integrated in cars, trucks, boats or other transport means.

The electrically conductive substrate comprising metal fibers, an oxidizing catalyst, a reducing catalyst and a NOx-adsorbing compound is hereafter referred to as "NOx-adsorber".

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During the loading step, the S-comprising compounds are oxidated and adsorbed. Usually, the adsorbed S-comprising compound is a sulfate. During the execution of this step, also NOx from the combustion  
5 reaction is oxidized, essentially to NO<sub>2</sub>. This NO<sub>2</sub>, and possibly also the remaining NOx, is adsorbed by the NOx-adsorbing compound as inorganic nitrates.

During the desulfation step, which is done periodically, the adsorbed S-comprising compounds, usually sulfates will become unstable and  
10 decompose into SO<sub>3</sub> and the NOx-adsorbing compound. These NOx-adsorbing compounds may then retake their function of adsorbing compound for either NOx or S-comprising compounds, usually SO<sub>3</sub>. As subject of the invention, this temperature increase is obtained by  
15 providing electrical current to the electrical conductive substrate, which is heated due to the Joule-effect.

By providing the electrical current to the electrical conductive substrate the temperature of the substrate is increased above the decomposition  
20 temperature of the adsorbed S-comprising components. An advantage is that the temperature may be increased to more than 700°C, which decomposes the S-comprising components, being trapped on the NOx-adsorber, independent of the combustion process. So the "S-poisoning" of the NOx-adsorber is limited or reversed when the substrate is heated  
25 above the decomposing temperature of the S-comprising components. The use of more S-rich diesel may be tolerated by a process comprising an NOx-adsorber as subject of the invention, being able to execute the process as subject of the invention.

30 The desulfation step of the process may be done while exhaust gasses pass through the substrate (hereafter referred to as "on-line"), or the exhaust gasses are prevented to pass through the electrically conductive substrate (hereafter referred to as "off-line"). The latter off-

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line situation is to be preferred. The desulfatation step is preferably done when the capacity or efficiency of the NO<sub>x</sub>-adsorber becomes too small.

5 When the desulfatation step is executed, also a desadsorption and reducing step of the N-comprising compounds is done, referred to as "desadsorption and reducing step".

10 Additional desadsorption and reducing steps, without effecting a desulfatation of the NO<sub>x</sub>-adsorber, may be done periodically in order to release the N-comprising compounds, usually nitrates, on the NO<sub>x</sub>-adsorber. The desadsorption and reducing steps of the adsorbed nitrates to N<sub>2</sub> may be done on-line or off-line. The desadsorption and reducing steps of the N-comprising compounds are done periodically, preferably  
15 when the NO<sub>x</sub>-adsorber is near its saturation point.

20 The time and frequency of executing a loading step, a desulfation step or a desadsorption and reducing step of the N-comprising compounds, may be preset or calculated, taking the combustion conditions into account, or may depend on appropriate measurement e.g. downstream the electrically conductive substrate. Also the time of electrically heating the electrically conductive substrate may be preset or calculated, taking the S-load of the NO<sub>x</sub>-adsorber into account. To maximize NO<sub>x</sub>  
25 conversion efficiency, the storage capacity and frequency of regeneration must be optimized during the design of the NO<sub>x</sub>-adsorber. Typically capacity of Barium adsorbers in the fresh state amounts to around 2g NO<sub>x</sub> per liter of catalyst volume. Depending on the engine emissions, catalyst size and condition, and the desired NO<sub>x</sub> reduction,  
30 regeneration must be performed every 30-120 seconds. The duration of NO<sub>x</sub> adsorber regeneration is short, between one and a few seconds, e.g. 5 seconds.



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The desadsorbtion and reducing step may be done by appropriate motor management, providing hydrocarbons and/or CO to the NOx-adsorber. The initiation of the desadsorbtion and reducing step may be provided by a diesel combustion under rich combustion circumstances. These  
5 rich combustion circumstances provide the necessary hydrocarbons and/or CO for the reduction of the adsorbed N-comprising compounds, and increasing the temperature of the exhaust gasses, and so of the N-comprising compounds, above the desadsorbtion temperature of the N-comprising compounds adsorbed on the NOx-adsorber. More diesel is  
10 provided to the combustion reaction. Possibly, electrical current is provided to the electrically conductive substrate of the NOx-adsorber, in order to increase the temperature of the NOx-adsorber, so assisting the desadsorbtion of the N-comprising compounds. Since the temperature is not to be as high as necessary to release the adsorbed S-comprising  
15 compounds, less current is necessary.

Alternatively, CO and hydrocarbons may be provided by partially combusting soot, trapped by a soot trap which is installed upstream of the NOx-adsorber.  
20 Preferably, an electrically regeneratable metal fiber soot filter, being part of the combustion system, is installed upstream the NOx-adsorber. Most preferably, this electrically regeneratable metal fiber soot filter is installed close to the electrically conductive substrate of the NOx-adsorber, e.g. both the electrically regeneratable metal fiber soot filter  
25 and the electrically conductive substrate facing one to the other. The electrically regeneratable metal fiber soot filter will be loaded with soot after a certain period of time, this is during the loading step. During regeneration of the electrically regeneratable metal fiber soot filter, electrical current is provided to the electrically regeneratable metal fiber  
30 soot filter, which, due to the Joule effect, will be heated above the ignition temperature of the soot. Hydrocarbons and CO may be obtained by combustion of the soot and SOF are vaporized.  
The hydrocarbons, CO and SOF are used as reductans during the reduction reaction of the decomposed N-comprising compounds

adsorbed on the off-stream NOx-adsorber, providing N<sub>2</sub>. Due to the ignition and combustion of the soot, the NOx-adsorber, positioned in the direct vicinity of the electrically regeneratable metal fiber soot filter will be heated to a certain extend by heated exhaust gasses passing  
5 through the electrically conductive substrate or via radiation from the electrically regeneratable metal fiber soot filter.

Possibly, the electrical conductive substrate may additionally be heated, if necessary, using electric current passing through the substrate during desadsorption and reduction of the adsorbed N-comprising compound.  
10 Since the temperature is not to be as high as necessary to release the adsorbed S-comprising compounds, less current is necessary.

In case the desadsorption of the NOx-adsorber is to be executed more frequently than the regeneration of the electrically regeneratable metal fiber soot filter, additional desadsorbing and reducing steps may be  
15 executed, using combustion under rich combustion circumstances.

The management (e.g. duration and frequency of steps, and if necessary additional motor management) of these steps of the process, being the desadsorbition and reduction of the N-comprising components, desulfation step, and possibly the regeneration step of the soot filter,  
20 can easily be automated, using appropriate electrical equipment and components, such as integrated circuits, connected to the electrically conductive substrate and possibly to the electrically regeneratable metal fiber soot filter, or to other elements of the combustion system.

25 As subject of the invention the NOx-adsorber comprises an oxidizing catalyst, e.g. Pt or Pd. The NOx-adsorber further comprises a reducing catalyst, e.g. Rh. The NOx-adsorber also comprises an NOx-adsorbing compound, comprising alkali-earth metals, such as Mg, Ca, Sr or Ba, alkali metals such as Li, Na, K, or Cs or rare earth metals such as Y, La  
30 or other lanthanides. Those NOx-adsorbing compounds are preferably present as salt such as oxides. Preferably BaO is used.

Those 3 materials, hereafter referred to as "active elements", may be present homogeneously over the depth of the substrate, through which the exhaust gasses are to flow. Alternatively, each active element may be present at preferred depth of the substrate. They may be provided on the substrate using presently known coating techniques, such as CVD-techniques, sol-gel techniques or by using wash coats. The catalyst support and the active elements can be provided on the substrate using precipitation and coprecipitation techniques, e.g. using washcoats. The washcoats can be applied as an aqueous slurry, by a continuous or non-continuous dipping process, washcoats can also be applied using a spray process. The catalyst support and active elements can also be provided on the substrate using a sol-gel preparation. If the above techniques only where used to ad a support on the substrate, CVD techniques or other know coating techniques can be used to provide the substrate/support with the active elements.

Some metal fleece surface treatments may be used prior to the application of the above described techniques, and some heat treatments can be applied afterwards.

The electrically conductive substrate preferably comprises metal fibers. These metal fibers may differ in alloy, length and diameter according to the required properties of the substrate. Preferably, the substrate consists of a metal fiber fleece. A sintered metal fiber fleece is most preferred. The weight, air permeability, thickness, electrical surface resistance, surface density and/or porosity may be varied to provide the required substrate properties. The electrically conductive substrate may further comprise other heat resistant materials and fibers, such as ceramic fibers.

The invention further relates to a NOx-adsorbing element able to perform this process as subject of the invention.

An NOx-adsorbing element as subject of the invention comprises an electrically conductive substrate, which comprises metal fibers. In the

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scope of the present invention, metal fibers are to be understood as all kinds of metal fibers, preferably stainless steel fibers. The alloy of metal or steel may be chosen depending on the temperature range which is to be withstand by the metal fibers. Stainless steel fibers of AISI alloys of the 300- or 400 series, or alloys such as Inconel® are to be preferred. In case high temperatures (e.g. above 700°C) are to be withstand during execution of the desadsorbition and reducing steps, alloys comprising Fe, Al and Cr are preferred, such as Fecralloy®. The fibers may be obtained by any presently known production method, such as bundle drawing or shaving. Fiber equivalent diameters between 1 and 100 µm are to be used, preferably between 2 and 50 µm, e.g. between 12 and 35 µm such as 12, 17 and 22 µm. Preferably the metal fiber fleece is sintered using appropriate sintering circumstances, according to the alloy used. Preferably, the metal fibers are obtainable by bundle drawing or coil shaving. The latter is described more in detail in WO97/04152.

Equivalent diameter is to be understood as the diameter of a radial cut of an imaginary round fiber, having an identical surface as the radial cut of the fiber under consideration.

The substrate comprises or preferably even consists of metal fibers. A 100% metal fiber fleece is preferably, possibly sintered. Such electrically conductive substrate may further comprise thermally resistant e.g. ceramic particles or thermally resistant e.g. ceramic fibers. The electrical resistance can be varied over the surface of the substrate, although preferably, this electrical resistance is identical over the surface of the substrate and not directionally dependent.

In case an electrically regeneratable metal fiber soot filter is installed upstream the NO<sub>x</sub>-adsorber, the electrically regeneratable metal fiber soot filter preferably comprises or even consists of metal fibers. A 100% metal fiber fleece is preferably, possibly sintered. Such electrically regeneratable metal fiber soot filter may further comprise thermally

resistant e.g. ceramic particles or thermally resistant e.g. ceramic fibers. The electrical resistance can be varied over the surface of the electrically regeneratable metal fiber soot filter, although preferably, this electrical resistance is identical over the surface of the electrically  
5 regeneratable metal fiber soot filter and not directionally dependent.

Metal fibers used to provide electrically regeneratable metal fiber soot filter may be of the same of a different type as the metal fibers used to provide the electrically conductive substrate of the NO<sub>x</sub>-adsorber. The  
10 weight, air permeability, thickness, electrical surface resistance, surface density and/or porosity of the electrically conductive substrate may be varied to provide the required substrate properties.

In order to be able to supply electrical current to the electrically  
15 conductive substrate, the electrically conductive substrate is provided with at least two contact bodies, via which the electrically conductive substrate may be connected by means of current supply cables with an electrical power system, e.g. a battery and/or an integrated circuit, periodically switching the electrical current in order to execute the  
20 decomposition step of the S-comprising compounds of the NO<sub>x</sub>-adsorber.

This contact body divides in a proper way the electric current over the electrically conductive substrate. Preferably, these contact bodies are  
25 metal foils, e.g. Ni-foil or metal woven meshes, preferably sintered at two ends of the electrically conductive substrate. Alternatively, the contact bodies are thermally sprayed on the electrically conductive substrate. The current supply cables are connected to the contact bodies by welding (e.g. spot-welding), thermally spraying, sintering or by  
30 means of bolts and nuts.

Identical or similar contact bodies may be provided to the electrically regeneratable metal fiber soot filter, if one is installed upstream of the electrically conductive substrate.

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5 An NOx-adsorbing element further comprises a fixing means, which is to keep the electrically conductive substrate in place. Preferably, the electrically conductive substrate is electrically insulated from the fixing means, or the fixing means itself is provided out of electrically insulating material. Possibly, if an electrically regeneratable metal fiber soot filter is present, this electrically regeneratable metal fiber soot filter may be fixed by the same fixing means as the one keeping the electrically conductive substrate in place.

10

15 A number of NOx- adsorbing elements may be assembled to a NOx- adsorbing unit, in order to provide sufficient electrically conductive substrate to the combustion system. Each NOx- adsorbing element separately, or a group of NOx- adsorbing elements together are located in a housing. Possibly the electrically regeneratable metal fiber soot filter or filters are located in the same housing. Possibly, the electrically regeneratable metal fiber soot filter or filters are positioned near the electrically conductive substrate or substrates and are fixed by the same fixing means.

20

25 In case the desadsorption and reducing steps of the N-comprising compounds and/or the desulfatation step is executed off-line, a NOx- adsorbing unit further comprises an appropriate valve system, which shut of the NOx- adsorbing element or elements during the execution of the different steps. This valve system may be controlled by the same integrated circuit as the one which controls the provision of electric current to the NOx-adsorbing element.

25

30 The management of such NOx-adsorbing unit, possibly with integrated electrically regeneratable metal fiber soot filter, can easily be automated, using appropriate electrical equipment and components, such as integrated circuits, connected to the electrically conductive substrates, the valve system and possibly to the electrically regeneratable metal

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fiber soot filters or measurement equipment controlling the process parameters in the NOx-adsorbing unit (e.g. pressures, temperatures, NOx-concentrations, ...).

5 The NOx-adsorbing unit is then a part of the combustion system as subject of the invention, which further comprises a combustion unit and an exhaust system, of which the NOx-adsorbing unit, and so the NOx-adsorbing elements, are part of.

10 **Brief description of the drawings.**

The invention will now be described into more detail with reference to the accompanying drawings wherein

- FIGURE 1, and FIGURE 2 show a detail of NOx-adsorbing elements as subject of the invention.
- 15 - FIGURE 3 is a section of an NOx-adsorbing element as subject of the invention.
- FIGURE 4 and FIGURE 5 show contact bodies of an NOx-adsorbing element as subject of the invention.
- FIGURE 6 shows an alternative cross section of an NOx-adsorbing element as subject of the invention.
- 20 - FIGURE 7 shows schematically a NOx-adsorbing element comprising additionally an electrically regeneratable metal fiber soot filter;
- FIGURE 8 shows schematically an NOx-adsorbing unit as subject of the invention.
- 25

**Description of the preferred embodiments of the invention.**

Preferred NOx-adsorbing elements as subject of the invention are shown in FIGURE 1, 2 and 3.

30

A number of NOx-adsorbing elements 11 are stacked one on top of the other. They all have a ring-like shape. A perforated metal tube 12 is positioned inside the inner opening 13 of the NOx-adsorbing element.

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Between each NOx-adsorbing element, a disc-like SiO<sub>2</sub> felt material 14 is positioned to thermally insulate the different NOx-adsorbing elements from each other. At both ends of the NOx-adsorbing unit, a metal plate 15 is fixed against the upper and lower NOx-adsorbing element e.g. as shown in FIGURE 1 by means of a screw 16, which pushes the plate towards the NOx-adsorbing element. Between this plate 15 and the upper or lower NOx-adsorbing element, another disc-like SiO<sub>2</sub> felt material 14 is positioned. A spring may be introduced between the plate 15 and the crew 16 to absorb thermal expansions of the stack of NOx-adsorbing elements 11.

When this NOx-adsorbing unit is used, preferably the exhaust gas flows in from the outer side of the NOx-adsorbing elements (indicated with arrow 17), through the electrically conductive substrate 18 through the perforations of the metal tube 12, to the further elements of the combustion system, of which it is part, as indicated with arrow 19. Alternatively, the gas flow may be directed in the other direction, being an "inside-out" flow.

Taking each NOx-adsorbing element of the present embodiment into consideration, a metal fiber fleece is used as electrically conductive substrate 18. The NOx-loaded gas flows in via the inflow side 20, through the metal fiber fleece, via the outflow side 21 of the metal fiber fleece to the further combustion system. The metal fiber fleece is connected via two contact bodies 22 and 23 to an electric circuit 24, providing electrical current to the metal fiber fleece in order to heat the electrically conductive substrate. The metal fiber fleece is preferably pleated in such a way that the thermal radiation heat, generated by the pleats 25, radiates to the adjacent pleats, as indicated by arrows 26. An important reduction of electrical power is obtained using this radiation heat to increase the temperature of the electrically conductive substrate during execution of the desadsorbition and reducing steps of the process as subject of the invention.



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As electrically conductive substrate, a sintered metal fiber fleece comprising three layers of stainless steel fibers is used. A first layer comprises 600 g/m<sup>2</sup> of Fecralloy® fibers with equivalent diameter of 17 µm. A second layer of Fecralloy® fibers is applied on top of the first layer. This layer comprises 250 g/m<sup>2</sup> of fibers with equivalent diameter of 22 µm. A third layer of Fecralloy® fibers is applied on top of the second layer, having fibers with equivalent diameter of 35 µm. This third layer comprises 600 g/m<sup>2</sup> fibers.

10 An oxidizing catalyst Pt, and a reducing catalyst Rh is provided. BaO is preferably used as NOx-adsorbing compound.

The set-up of a preferred embodiment of the NOx-adsorbing element is shown in FIGURE 2. A fixing means, being a flank 28 of the NOx-adsorbing element comprises a metal rim 29, to which a wire mesh 30 is spot welded on several spots 31. A fine layer of ceramic material 32 was sprayed on the electrical and thermal insulating side 33 of the flank. A relatively thick layer of ceramic adhesive 34 was applied on this mesh and the electrical and thermal insulating side 33, before the metal fiber fleece 18, loaded with an oxidizing catalyst, a reducing catalyst and an NOx-adsorber, was adhered to this ceramic adhesive 34, which comprises more than 10% of weight of short metal fibers. The addition of such short metal fibers, having an equivalent diameter in the range of 1 to 150 µm and a length over diameter (L/D) ratio in the range of more than 5, improves the ductility and thermal stability of such ceramic glues.

To improve the resistance to the mechanical tension, due to the fixation of the different elements on top of each other by screw 16, several studs 35 may be welded to the upper and lower rim of each NOx-adsorbing element.

Turning now to the contact bodies 22 and 23 of the preferred embodiment as shown in FIGURE 4 and FIGURE 5, a fine Ni-sheet 36

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was sintered to the ends of the metal fiber fleece. Both contact bodies were brought together and fixed to an insulating plate 37, e.g. a mica-plate by means of two bolts 38 and 39. In order to avoid electrical contact between contact body 22 and bolt 38, and between contact body  
5 23 and bolt 39, two mica sheets were inserted between the insulating plate 37 and the contact bodies 22 and 23.

An alternative set-up is shown in FIGURE 5. An identical set-up as in FIGURE 4 is used, but the contact body 22 is shaped in such a way that  
10 no material of this contact body 22 is present at behind bolt 38, fixing the contact body 23 to the insulating plate 37. Identically, the contact body 23 is shaped in such a way that no material of this contact body 23 is present at behind bolt 39, fixing the contact body 22 to the insulating plate 37. Using such contact bodies, the use of two mica plates 40 may  
15 be avoided, which may simplify the construction of the NOx-adsorbing element. The electric connection of the contact bodies to the power supply or an integrated circuit, may be done by a current supply cable, connected to e.g. the used bolts and nuts.

20 An alternative cut according to BB' is shown in FIGURE 6. The perforated tube in this embodiment has an elliptic section. Also here, the metal fiber fleece is pleated according to pleating lines, which enables radiation from one pleat to another during the increasing of the temperature for the desulfatation steps of the adsorbed S-comprising  
25 compounds as subject of the invention.

When NOx-adsorbing elements as in FIGURE 1 are used, the NOx- and S-loaded exhaust gasses are supplied to the NOx-adsorbing element. The oxidizing catalyst oxidizes the NOx and the oxidated products are  
30 trapped or adsorbed by the NOx-adsorber, forming N-comprising compounds.

In the preferred embodiment, Pt is used as an oxidizing catalyst. NOx is oxidized to a large extend to NO<sub>2</sub>. NO<sub>2</sub>, and the remaining NOx is than

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adsorbed on by the NOx-adsorbing compound as N-comprising compounds. Preferably the NOx-adsorbing compound is BaO, so Ba(NO<sub>3</sub>)<sub>2</sub> is provided.

5 During desadsorption of the N-comprising compounds, these compounds become unstable and are released again as NO<sub>2</sub> and possibly NOx. This may be obtained by running the combustion process for a short period in time under rich combustion circumstances. Hydrocarbons and CO is then provided to the NOx-adsorber. Possibly,  
10 some electric current may be provided to the electrically conductive substrate to increase its temperature (e.g. above 200°C) due to Joule-effects. This helps to proceed the desadsorption and reduction step.

These desadsorbed N-comprising compounds, usually NO and NO<sub>2</sub>, are  
15 reduced over the reducing catalyst, preferably Rh, providing N<sub>2</sub>, and making use of the hydrocarbons and/or CO as reductance.

The exhaust gasses comprise also amounts of S-comprising elements, which are at least partially oxidized by the oxidizing catalyst to oxidized  
20 S-comprising compounds, usually SO<sub>3</sub>, when the exhaust gasses pass through the electrically conductive substrate. This oxidized S-comprising compound is then at least partially adsorbed by the NOx-adsorbing compound as adsorbed S-comprising components, usually sulfates.

25 When BaO is used, BaSO<sub>4</sub> is provided. During a desulfation step, the temperature of the electrically conductive substrate is preferably increased above 700 °C. The S-comprising compounds, adsorbed on the NOx-adsorber which is so-called poisoned by the S-elements, become unstable and the adsorbed S-comprising compounds are  
30 decomposed, usually as SO<sub>3</sub>. The desulfation of NOx adsorbers requires temperatures between 500-700°C. E.g. a desulfation of Barium-based NOx-adsorbers is achieved at at least 650°C.

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5 In case BaO is used, SO<sub>3</sub> has been adsorbed as BaSO<sub>4</sub>. The temperature is to increase preferably to more than 700°C to release SO<sub>3</sub> again. This may be realized since the substrate is electrically conductive, and electric current is provided to the substrate to heat this substrate due to its Joule effect.

10 For a person skilled in the art, it is clear that a NO<sub>x</sub>-adsorbing unit as subject of the invention comprises appropriate valve systems to shut down one or more NO<sub>x</sub>-adsorbing elements during desadsorption and reduction of the N-comprising components and/or decomposition of the adsorbed S-comprising compounds, in case one of the steps is done off-line.

15 FIGURE 7 shows a preferred embodiment of NO<sub>x</sub>-adsorbing element as subject of the invention, comprising a NO<sub>x</sub>-adsorber and an electrically regeneratable metal fiber soot filter. The NO<sub>x</sub>-adsorbing element has a ring-like structure. FIGURE 7 shows a section of the NO<sub>x</sub>-adsorbing element, perpendicular to its axis 71.

20 An electrically regeneratable metal fiber soot filter 72 is provided, being a sintered metal fiber fleece, having an essentially rectangular shape. This rectangle is pleated parallel to one pair of edges of the rectangle, so providing the other pair of edges a waves shape. The two edges parallel to the pleating lines are brought together at each edge, a  
25 contact body 73 and 74 is provided.

30 An electrically conductive substrate 75 is provided, being a sintered metal fiber fleece, having an essentially identical shape as the electrically regeneratable metal fiber soot filter 72. This electrically conductive substrate 75 is pleated to an essentially identical shape as the electrically regeneratable metal fiber soot filter filter 72. The electrically conductive substrate 75 is positioned downstream of the electrically regeneratable metal fiber soot filter 72. To both edges of the

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electrically conductive substrate, two contact bodies 76 and 77 may be provided.

5 The metal fiber fleeces are preferably pleated in such a way that the thermal radiation heat, generated by the pleats 78, radiates to the adjacent pleats, as indicated by arrows 79. An important reduction of electrical power is obtained using this radiation heat to increase the temperature of the electrically regeneratable metal fiber soot filter and electrically conductive substrate during execution of the regenerating,  
10 respectively desulfation step and/or releasing and reducing steps of the process as subject of the invention. Since the electrically regeneratable metal fiber soot filter 72 is situated close to the electrically conductive substrate 75, thermal energy will radiate from the electrically regeneratable metal fiber soot filter 72 to the electrically conductive substrate 75, so partially increasing the temperature of the electrically  
15 conductive substrate during regeneration of the filter.

As electrically conductive substrate, a sintered metal fiber fleece comprising three layers of stainless steel fibers is used. A first layer  
20 comprises 600 g/m<sup>2</sup> of Fecralloy® fibers with equivalent diameter of 17 µm. A second layer of Fecralloy® fibers is applied on top of the first layer. This layer comprises 250 g/m<sup>2</sup> of fibers with equivalent diameter of 22 µm. A third layer of Fecralloy® fibers is applied on top of the second layer, having fibers with equivalent diameter of 35 µm. This third  
25 layer comprises 600 g/m<sup>2</sup> fibers.

An oxidizing catalyst Pt, and a reducing catalyst Rh is provided. BaO is preferably used as NOx-adsorbing compound.

30 A second metal fiber fleece is used as an electrically regeneratable metal fiber soot filter, which traps the soot particulate and SOF before the exhaust gas is to flow through the electrically conductive substrate. The soot and SOF, retained by this metal fiber fleece, will be released,

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e.g; vaporized as far as SOF is concerned, or combusts, as far as soot is concerned, and provide hydrocarbons and CO to the part of the combustion system downstream of this metal fiber fleece, being an electrically regeneratable metal fiber soot filter.

5

A sintered metal fiber fleece comprising three layers of stainless steel fibers is preferably used. A first layer comprises 600 g/m<sup>2</sup> of Fecralloy® fibers with equivalent diameter of 17 µm. A second layer of Fecralloy® fibers is applied on top of the first layer. This layer comprises 250 g/m<sup>2</sup> of fibers with equivalent diameter of 22 µm. A third layer of Fecralloy® fibers is applied on top of the second layer, having fibers with equivalent diameter of 35 µm. This third layer comprises 600 g/m<sup>2</sup> fibers.

10

15

A soot retention of 91% was obtained, using a stainless steel fleece, having a porosity of 85%.

The soot was so-called depth filtered. This is to be understood as the fact that soot particles were trapped through the whole depth of the filter. SOF is present in its liquid phase on the soot particulates.

20

The contact bodies 73, 74, 76 and 77 used to provide electric current to the electrically regeneratable metal fiber soot filter 72, and the electrically conductive substrate 75, are identical to the one as indicates 22 and 23 in FIGURE 3.

25

The contact bodies 73, 74, 76 and 77 are connected to a power supply and/or an appropriate integrated circuit 70.

30

Both the electrically regeneratable metal fiber soot filter 72 and the electrically conductive substrate 75 are integrated in a NO<sub>x</sub>-adsorbing element in a similar way as shown in FIGURE 2.

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When this NO<sub>x</sub>-converting unit is used, preferably the exhaust gas flows in from the outer side of the NO<sub>x</sub>-adsorbing element, through the electrically regeneratable metal fiber soot filter 72, through the electrically conductive substrate 75, out of the NO<sub>x</sub>-adsorbing element.

5

During a loading step, soot and SOF are retained by the electrically regeneratable metal fiber soot filter 72. The exhaust gasses, still loaded with NO<sub>x</sub> is then provided to the electrically conductive substrate 75.

10

The oxidizing catalyst oxidizes the NO<sub>x</sub> and the oxidated products are trapped or adsorbed by the NO<sub>x</sub>-adsorber, forming N-comprising compounds, usually nitrides. S-comprising compounds are adsorbed as well.

15

In the preferred embodiment, Pt is used as an oxidizing catalyst. NO<sub>x</sub> is oxidized to a large extent to NO<sub>2</sub>. NO<sub>2</sub>, and the remaining NO<sub>x</sub> is then adsorbed on by the NO<sub>x</sub>-adsorbing compound as N-comprising compounds. Preferably the NO<sub>x</sub>-adsorbing compound is BaO, so Ba(NO<sub>3</sub>)<sub>2</sub> is provided.

20

After a defined time period, the exhaust gas is preferably prevented to flow through the electrically regeneratable metal fiber soot filter 72 and the electrically conductive substrate 75. Electrical current is provided to the electrically regeneratable metal fiber soot filter via current supply cables and the contact bodies 76 and 77. The electrically regeneratable metal fiber soot filter 72 is heated unto a temperature up to 1000°C, but preferably in the range of 500°C to 600°C. The soot and the SOF, which was retained by the electrically regeneratable metal fiber soot filter 72, is combusted or vaporized, providing CO<sub>2</sub>, CO and hydrocarbon compounds.

25

30

Due to the increased temperature of the electrically regeneratable metal fiber soot filter 72, the electrically conductive substrate 75 is also heated, up to a temperature of more than 250°C. The N-comprising compounds become unstable and are released again as NO<sub>2</sub> and

possibly NOx. Thermal energy, radiated by this electrically regeneratable filter during regeneration is used. In case this temperature is not reached due to radiation of the electrically regeneratable metal fiber soot filter 72 during regeneration, additional electrical current may be supplied to the electrically conductive substrate 75.

These released products are reduced over the reducing catalyst, preferably Rh, providing N<sub>2</sub> while CO and hydrocarbon compounds, present due to imperfect combustion of the soot, being oxidized.

In case the electrically conductive substrate 75 comprise significantly amounts of S-comprising elements (e.g. due to combustion of S-rich diesel), periodically the temperature of the substrate is preferably increased above 700 °C. The obtained S-comprising compounds, usually sulfates, adsorbed on the NOx-adsorber, also become unstable and are being released as SO<sub>3</sub>. To obtain this temperature on the electrically conductive substrate 75, electrical current is provided to the electrically conductive substrate 75. In case BaO is used, SO<sub>3</sub> has been adsorbed as BaSO<sub>4</sub>. The temperature is to increase to more than 700°C to release SO<sub>3</sub> again. This may be realized when the substrate being electrically conductive, and electric current is provided to the substrate to heat this substrate due to its Joule effect.

Preferably this desulfation step is executed simultaneously with a regeneration of the electrically regeneratable metal fiber soot filter 72.

An NOx-adsorbing unit 88 is shown in FIGURE 8. As shown, several NOx-adsorbing elements 80 are stacked into stacks 87, which are in their turn located in a housing 86.

All NOx-adsorbing elements 80 have a ring-like shape. A perforated metal tube 81 is positioned inside the inner opening 82 of the NOx-adsorbing elements. Between each NOx-adsorbing element, a disc-like SiO<sub>2</sub> felt material 83 is positioned to thermally insulate the different NOx-adsorbing elements from each other.



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Several stacks are positioned in NOx-adsorbing unit 88. A valve system 84 is installed comprising one or several valves 85, which can shut off periodically one or more stacks, while other stacks are kept inline.

5 During this shut off, one or several NOx-adsorbing elements are to execute the desadsorption and reducing step, the desulfation step and possibly the regeneration step of a soot filter. The electric current supply to the different NOx-adsorbing elements 80 and the control of the valve system 84 may be done by one integrated circuit 86.

10

This NOx-adsorbing unit 88 may be used as a part of the exhaust system being part of a combustion system, e.g. a diesel engine.

**CLAIMS**

1. A method of desulfation of NOx-adsorbers in a diesel exhaust system, comprising the steps of
- 5       ▪ providing an electrically conductive substrate comprising metal fibers, an oxidizing catalyst, a reducing catalyst and a NOx-adsorbing compound;
- 10       ▪ executing a loading step, passing the exhaust gasses from said diesel exhaust system through said electrically conductive substrate, at least partially oxidizing S-comprising compounds and at least partially adsorbing said oxidized S-comprising compounds as adsorbed S-comprising compounds on said NOx-adsorbing compound;
- 15       executing a desulfation step by increasing the temperature of said electrically conductive substrate above the decomposition temperature of said adsorbed S-comprising compounds by providing electric current to said electrically conductive substrate.
2. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claims, said electrically conductive substrate is heated
- 20       above 700°C .
3. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claim 1 to 2, said process further comprising the step of providing an electrically regeneratable metal fiber soot filter
- 25       upstream from said electrically conductive substrate.
4. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claim 1 to 3, said process comprising the additional step of desadsorption and reducing N-comprising compounds, being
- 30       adsorbed by said NOx-adsorbing compound by providing hydrocarbons and/or CO for the reduction of the adsorbed N-comprising compounds, and increasing the temperature of said N-comprising compounds above the desadsorption temperature of said

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N-comprising compounds adsorbed on the NOx-adsorber during said loading step.

- 5 5. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claim 4, said hydrocarbons and/or CO being provided by regeneration of said electrically regeneratable metal fiber soot filter.
- 10 6. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claim 4 or 5, increasing temperature of said N-comprising compounds above the desadsorption temperature of said N-comprising compounds adsorbed on the NOx-adsorber during said loading step is obtained by providing electric current to said electrically conductive substrate.
- 15 7. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claim 1 to 6, said NOx-adsorbing compound comprising BaO.
- 20 8. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claims 1 to 7, said electrically conductive substrate is a sintered metal fiber fleece.
- 25 9. A method of desulfation of NOx-adsorbers in a diesel exhaust system as in claims 1 to 8, said metal fibers comprising Fe, Al and Cr.
- 30 10. An NOx-adsorbing element, comprising a substrate, an oxidizing catalyst, a reducing catalyst and a NOx-adsorbing compound, characterized in that said substrate being electrically conductive, said electrically conductive substrate comprising metal fibers.

11. An NOx-adsorbing element as in claim 10, said metal fibers metal fibers of said electrically conductive substrate comprising Fe, Al and Cr.
- 5 12. An NOx-adsorbing element as in claim 10 to 11, said electrically conductive substrate being a sintered metal fiber fleece.
13. An NOx-adsorbing element as in claim 10 to 12, said NOx-adsorbing compound comprising BaO.
- 10 14. An NOx-adsorbing element as in claim 10 to 13, said metal fibers having an equivalent diameter in the range of 1 to 100 $\mu$ m.
- 15 15. An NOx-adsorbing element as in claim 10 to 14, said metal fiber fleece being pleated.
16. An NOx-adsorbing element as in claim 10 to 15, said NOx-adsorbing element further comprising an electrically regeneratable metal fiber soot filter located upstream of said electrically conductive substrate.
- 20 17. An NOx-adsorbing element as in claim 16, said metal fibers of said electrically conductive substrate and metal fibers of said electrically regeneratable metal fiber soot filter being identical.
- 25 18. An NOx-adsorbing unit, comprising at least one NOx-adsorbing element as in claim 10 to 15.
19. An NOx-adsorbing unit, comprising at least one NOx-adsorbing element as in claim 16 to 17.
- 30 20. An NOx-adsorbing unit as in claim 18, said NOx-adsorbing unit comprising an integrated circuit, being connected to said electrically conductive substrates of said NOx-adsorbing elements.

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5

21. An NOx-adsorbing unit as in claim 19, said NOx-adsorbing unit comprising an integrated circuit, being connected to said electrically conductive substrates of said NOx-adsorbing elements.
22. An NOx-adsorbing unit as in claim 20 to 21, said NOx-adsorbing unit comprising a valve system.

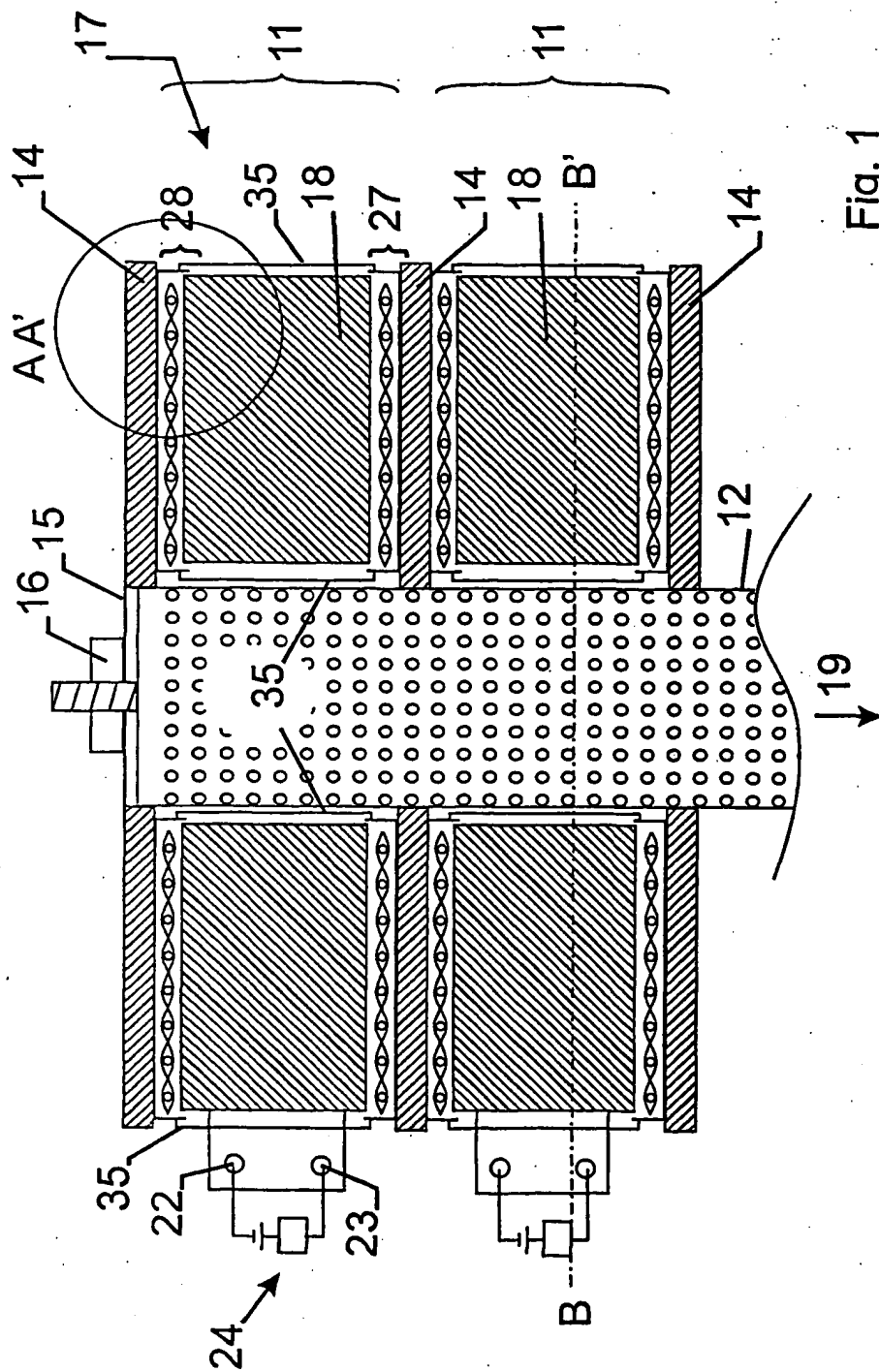


Fig. 1

- 2/5 -

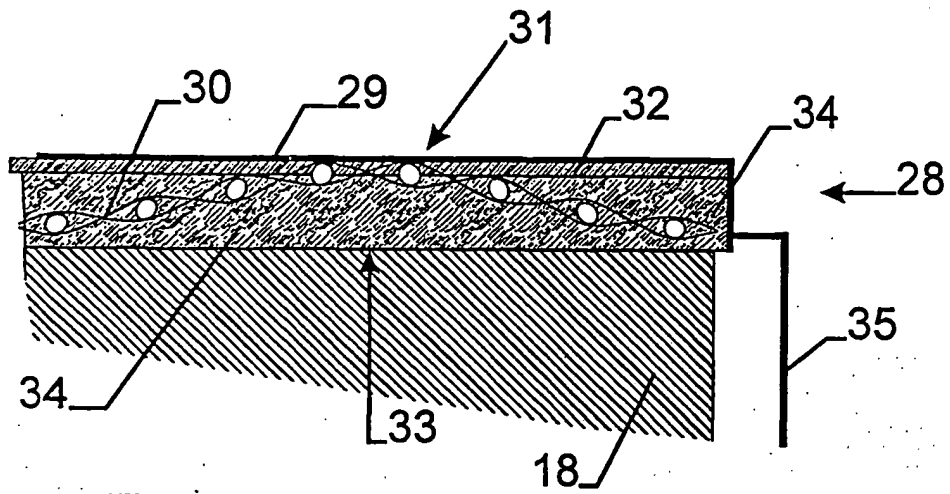


Fig. 2

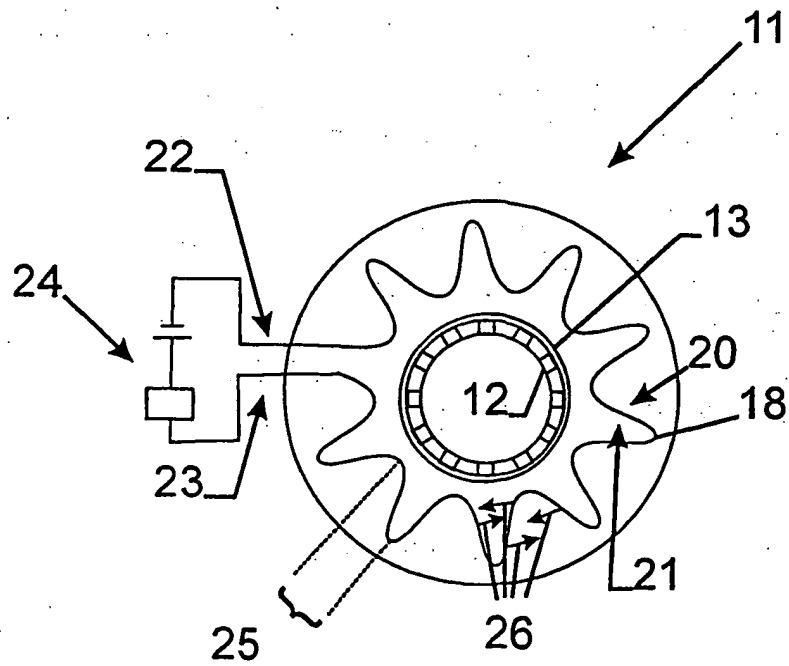


Fig. 3

- 3/5 -

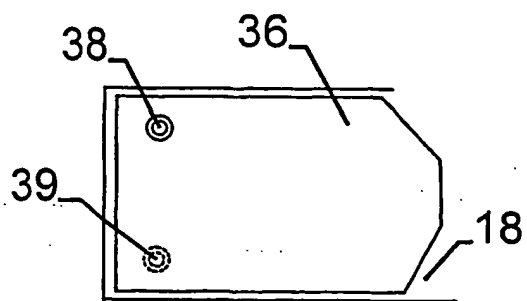


Fig. 4

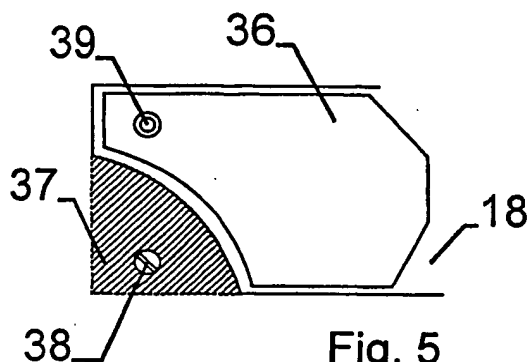
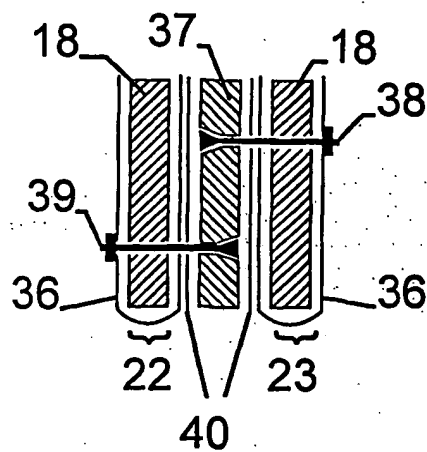


Fig. 5

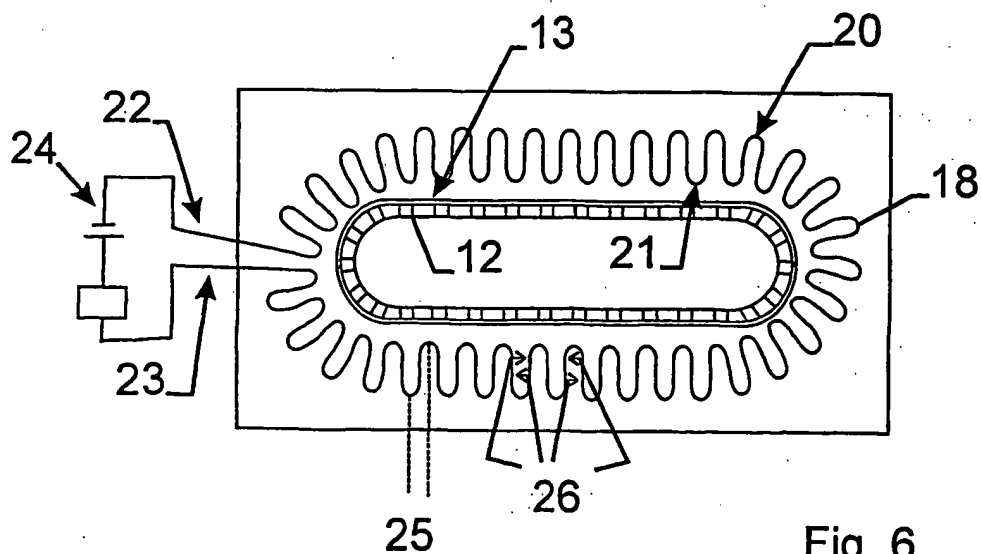
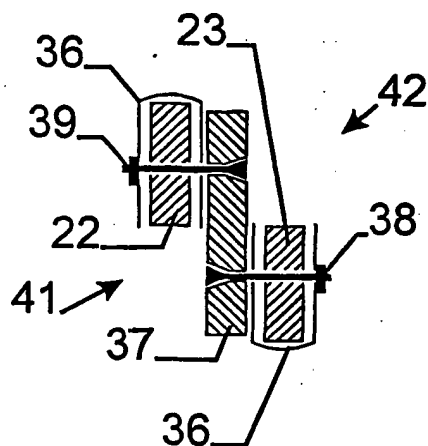


Fig. 6



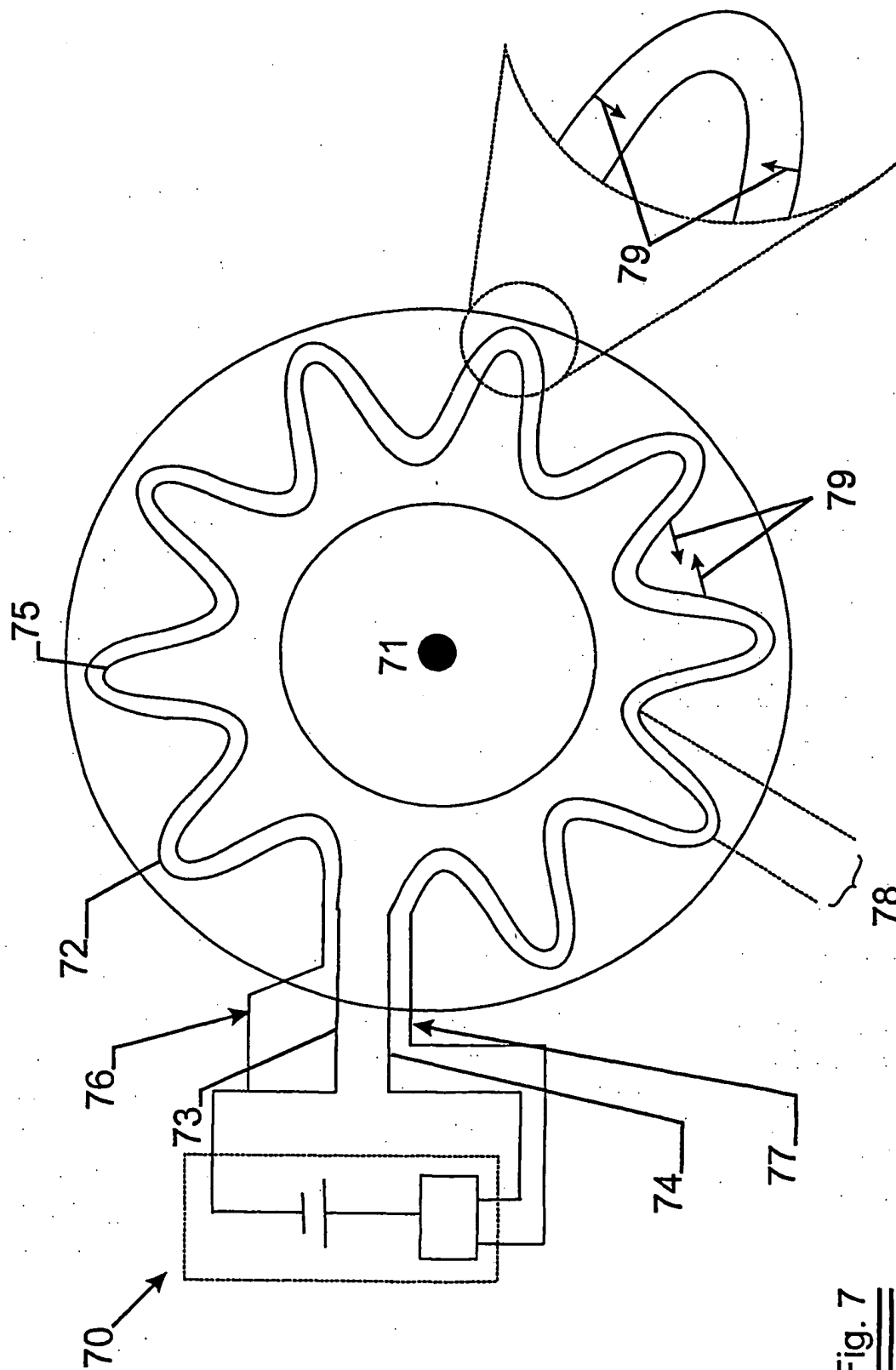


Fig. 7

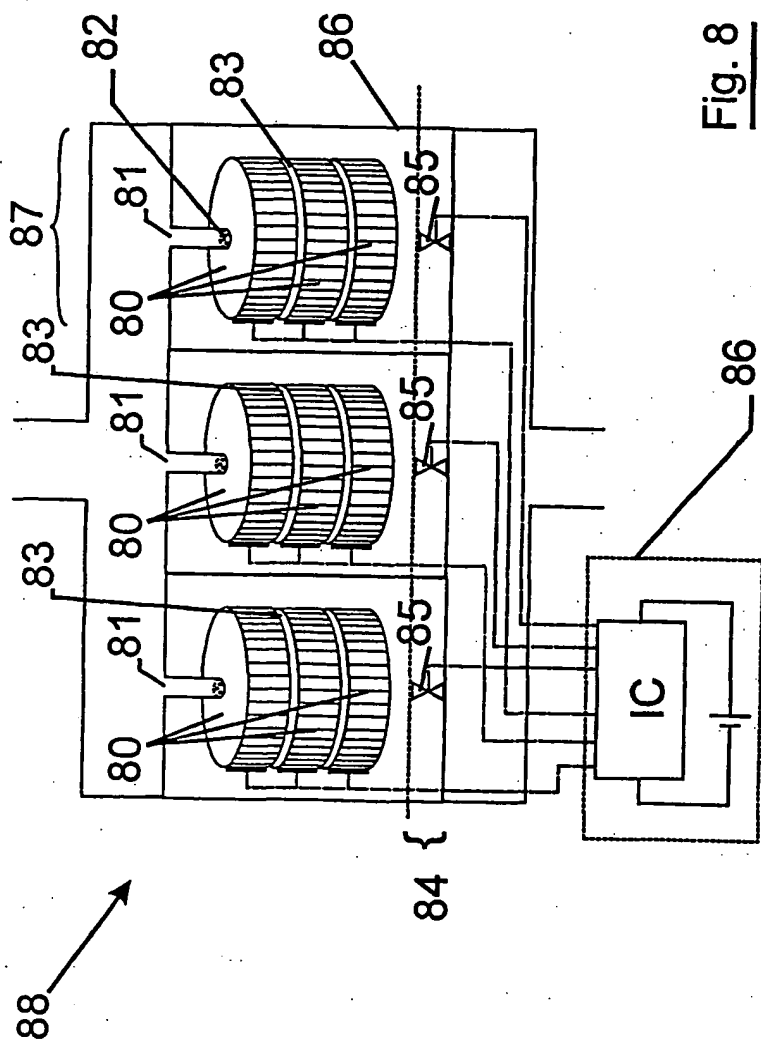


Fig. 8

International Application No  
PCT/EP 02/06249

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 F01N3/08 F01N3/20 B01D53/94 F01N3/027

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 F01N B01D F02D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 101 907 A (ISUZU CERAMICS RES INST CO LTD) 23 May 2001 (2001-05-23)	1,3-5,7, 8,10,12, 13,16-19
Y	paragraph '0014! - paragraph '0031!; figure 1	2,6,9, 11,14
Y	EP 0 764 455 A (NIPPON OIL CO LTD ;SINTOKOGIO LTD (JP)) 26 March 1997 (1997-03-26) page 3, line 31 -page 5, line 20; figures 2,5	2,6,9, 11,14
A	EP 1 072 764 A (RENAULT) 31 January 2001 (2001-01-31) the whole document	1,6,8,10
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 October 2002

Date of mailing of the international search report

04/11/2002

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## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 02/06249

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 636 770 A (TOYOTA MOTOR CO LTD) 1 February 1995 (1995-02-01) column 7, line 47 column 30, line 39 - line 56 column 31, line 26 column 23, line 5 - line 10 column 6, line 45	1,4

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/06249

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1101907	A	23-05-2001	JP	2000073739 A	07-03-2000
			EP	1101907 A1	23-05-2001
EP 0764455	A	26-03-1997	JP	9085027 A	31-03-1997
			JP	9085028 A	31-03-1997
			EP	0764455 A2	26-03-1997
			US	5800790 A	01-09-1998
EP 1072764	A	31-01-2001	FR	2796986 A1	02-02-2001
			EP	1072764 A1	31-01-2001
EP 0636770	A	01-02-1995	DE	69420488 D1	14-10-1999
			DE	69420488 T2	13-04-2000
			EP	0636770 A1	01-02-1995
			US	5483795 A	16-01-1996
			WO	9417291 A1	04-08-1994
			JP	2692380 B2	17-12-1997